REMOVAL OF SOLUBLE GASES (AND PARTICULATES) FROM AIR STREAMS
(With Special Reference to Fluorides)

by

Edward M. Berly, Melvin W. First and Leslie Silverman

Presented by
Melvin W. First

1. Introduction

The wide use of hydrofluoric acid in process metallurgy for beryllium, uranium and other metals prompted the New York Operations Office of the Atomic Energy Commission to request the Harvard Air Cleaning Laboratory to investigate methods of removal of fluorides from stack gases.

Hydrofluoric acid as a gas can be absorbed in conventional packed towers filled with Berl Saddles, Raschig Rings or similar materials to provide intimate mixing and absorbing surface for the gas stream and the counter-currently flowing solvent. Hydrofluoric acid exhibits such a strong affinity for water that it may be absorbed also in simple spray chambers using water as a scrubbing fluid.

Tests at the Harvard Air Cleaning Laboratory(1) showed that wetted fiber cells give high efficiency with aerosols containing 1) soluble acid mists and 2) soluble gases with low vapor pressures. The large wetted area represented by the fiber surface of even large diameter fiber packs presents a favorable situation for gas absorption.

The removal of particulates, i.e. fluoride mists and fume, is not readily accomplished in ordinary spray chambers or in towers filled with conventional packings because effective separation requires fine droplets (50 microns) or fine fibers (< 5 microns). Mechanical features limit the use of fine fibers to dry operations.

When fluorides are present in air or gas streams as a mixed gas, mist and fume, it is desirable to collect them simultaneously in a single unit if possible. Previous experiments with the wet cell washer indicated that

series of wet and dry, fibrous, deep bed filters were a suitable means of cleaning effluent gases containing soluble or reactive materials.

Inert particulates which may accompany the mist or soluble fume in small or large concentration will likewise be captured by the packing and may adhere to it and eventually plug the bed. Therefore, provisions must always be made for removing inert particulates early in the cleaning process, or for periodically cleaning or replacing those sections of packing which become plugged and useless.

Cleaning requirements (i,e. degree of efficiency required) may be considered under two categories; First, removal of low concentrations from stack gas effluents; the primary purpose here is the elimination or prevention of atmospheric contamination, second, scrubbing of process gases or off-gases containing sufficient material to make recovery and re-utilization economically desirable. In many instances it may be necessary to meet both requirements although gases which cause problems of atmospheric contamination only are generally too lean for recovery, concentration and purification. High collection efficiency is not always needed for the removal of offending material from stack gases. Generally, the intent is to reduce the effluent below a concentration which can produce a nuisance.

On the other hand, high efficiency is generally required for collecting products from process gases to prevent stack gas effluents from becoming neighborhood nuisances. In some cases, it may be desirable to break the process into two operations. In the first, the rich gases are recovered at high efficiency in a relatively few absorption steps and in the second the clean gases are further cleaned for discharge to the atmosphere; the recovered material in the latter process being discarded.

2. Experimental Equipment

An experimental multiple-stage wetted-cell washer of the type shown in

Figure 1 was used in all the tests. The unit will receive a variety of fiber filters placed at a 45° angle to the air stream. The coarse fiber wetted cells were followed by a droplet eliminator and fine fiber pads. The interior of the cabinet, including the filter frames, was coated with protective paint to reduce corrosion. The scrubbing liquor in the sump was recirculated and the fluoride concentration was allowed to increase to approximately 2%. Air was drawn into the unit by an exhauster on the exit side (washer under negative pressure). This type of equipment is not generally used for gas absorption, but has certain advantages over conventional tower construction. Increased capacity may be achieved by raising the number of filters in parallel in each stage.

For absorption of HF the selection of materials from which to make chemically resistant fibers is rather restricted. Fortunately, several plastics have excellent chemical resistance and are produced in a large number of fiber sizes. Saran and Dynel plastic fibers were investigated in this study. Both Saran and Dynel were obtained in the form of 2 to 6 inch long curled fibers which possess a degree of stiffness and resiliency not equalled by other synthetic fibers below 100 microns in diameter. At the time of this study Saran fibers were available in diameters of 27 microns and upward and for Dynel, 10 microns and up.

Previous work[1] with Fiberglas filters indicated that concurrent spraying permits higher gas velocities than are practical with countercurrent operation and reduced channeling results in better wetting of the packing. The absorption of high concentrations of HF from process gases can be accomplished directly by a system of countercurrent stages with concurrent spraying in each stage.

Wetting was accomplished with 6 suitably spaced flooding nozzles* per

* Clarage Company, No. O Flooding Nozzles

20 x 20 inch cross-section wet cell placed 6 inches upstream of the cell face. It is thus possible to have a 4 inch deep pad with adequate area and free of channeling. In conventional countercurrent towers, by contrast, height is often 5 times the diameter of the column to assure proper distribution of gas and liquid throughout the packing.

In most tests the scrubbing liquor was recirculated at the rate of 8 to 9.6 gallons per minute per 20 x 20 inch cell. This quantity of liquid is large in comparison with the amount of HF to be absorbed, hence the concentration of fluorides in the absorbing liquor remains substantially constant during passage through the wet cell. Because of this high liquid rate there is no appreciable temperature change due to heat of solution of HF in the scrubbing liquid.

Fine-spray nozzles* were also substituted for the first wet stage in order to determine the comparative efficiency of wetted fibers and fine spray droplets for the absorption of HF gas. When scrubbing dirty gases, a wetted Rockwell "Neva-Clog"** screen was substituted for the first wetted fiber stage.

Water was chosen as the absorbing liquor (in preference to an alkali such as NaOH) because (1) it has excellent affinity for HF even with as much as 2% dissolved HF, (2) it is low in cost and (3) an aqueous acid solution lends itself to easier economical recovery and concentration than alkaline salts.

3. Absorption of Hydrogen Fluoride Gas

Loadings of HF (as fluoride ion) ranging from 25 to 4000 mg. per cubic meter of air were absorbed at >99% efficiency with two wetted fiber cells in series using water containing 0 to 2% of fluoride as the scrubbing liquor (Test A, Table I).

* Bete Company Nozzle No. P40.

** A stainless steel perforated double plate screen with 125 staggered 0.045" diameter holes per square inch. Sheet thickness is 0.010 inches and the space between sheets, maintained by dimpling the sheets and spot welding, is 0.05".

Efficiency was independent of air flow rate over the range tested (i.e. 108 to 216 feet per minute superficial face velocity). A final dry pad increased over-all collection efficiency only a few tenths of one per cent since a dry filter can collect only those droplets small enough to penetrate the 6-bend zigzag eliminator.

Substituting a concurrent water spray (i.e. 6 No. O Clarage flooding nozzles without the fiber cell) for the first wet cell resulted in a significant decrease in total wet stage absorption (i.e. water sprays plus wet cell) from 99% and over to 95 or 96% but, in all cases except one, over-all efficiencies were 99% or better, indicating that for this equipment arrangement the final dry cells assume greater significance in the over-all performance. When the nozzles develop their full spray pattern (as they do when the wet cell is taken out) some droplets small enough to penetrate the coarse fiber cell constituting the second wet stage and the zigzag eliminator plates are formed. These are removed in the final fine-fiber dry pad.

When fine misting nozzles are substituted for the flooding nozzles a larger per cent of the spray is represented by very fine mist droplets, which penetrate the wet cells and eliminator. Using 6 and 9 misting nozzles as the first wet stage and a one inch pleated Saran fiber filter wetted by spray carry-over as the second, over-all efficiencies (including the dry pad) were from 86.2 to 95.5%, indicating that a significant number of mist droplets fine enough to penetrate two inches of 44 micron dry fibers were formed by the fine spray nozzles.

For a given volume of scrubbing liquor fine droplets produce most rapid equilibrium, but the complete removal of these fine droplets of hydrofluoric acid presents an additional problem. In general, for the absorption of a material as readily soluble as HF, coarse flooding nozzles or other devices which do not produce fine droplets are to be preferred from the standpoint of simplicity of equipment and low air flow resistance.

When the first wet stage is 2.3 square feet of Neva-Clog filter screen wetted with 5 flooding nozzles, scrubbing efficiency was found to increase with increasing water rate up to 92% at 4.4 gallons per minute per square foot of screen.

With high loadings (0.1 to 2.0 grams per cubic meter) of two typical inert mineral dusts (talc and silica), efficiency of the Neva-Clog screen was 79.0 to 87.2% when wetted with 3 gallons per minute per square foot of screen (Table II).

4. Removal of Particulates. (Mists and Fumes)

An aqueous fluoride mist aerosol was prepared from a 10% solution of NH_4FHF by aspiration. It had a median size by weight of 4.4 microns and a geometric standard deviation of 7.9, indicating a wide range of sizes about the median.

A single stage of one wetted Neva-Clog screen collected 70.2% of the fluoride mist, at a superficial face velocity of 108 feet per minute and 91.2% at double this velocity, indicating that impaction is the principal removal mechanism for droplets in this size range. A Neva-Clog screen followed by a 78 micron diameter wetted Saran pad and a 44 micron diameter dry Saran pad gave over-all efficiencies of 92 and 94.4% at 108 and 216 feet per minute face velocity, respectively; again indicating by a greater collection efficiency at the higher flow rate that the principal collection mechanism for the mist droplets is impaction. Substituting 6 misting nozzles for the Neva-Clog screen reduced wet stage efficiency from 87 and 89% to 74 and 83% at 108 and 216 feet per minute face velocity, respectively, but efficiency of the over-all system was not affected by the change in the first wet stage indicating that the final dry pad was carrying a greater proportion of the load.

With 29 micron Saran fibers in the final dry pad over-all efficiency

increased to 96.3%; and with three Saran fiber stages (two wet cells containing 78 micron diameter fibers and a dry pad containing 29 micron diameter fibers) efficiency rose to 98.1%. (Test B, Table I)

Although glass fibers deteriorate rapidly under the action of HF it was felt that if placed following the final dry Saran pad they would last long enough to indicate what sizes and weights of fibers are required to give virtually complete removal of the fluoride mist. Therefore, the following glass fibers were added downstream of the 27 micron Saran pad; (1) 1/2 inch thickness of resin bonded 3 micron glass fibers (PF 105), (2) 1/4 inch of 1 micron fibers (XAA) and (3) a second 1/2 inch layer of 3 micron resin bonded fibers. This pad gave virtually complete removal of bifluoride mist but began to plug rapidly after a few hours of use. Nevertheless, these tests demonstrated that high efficiency removal of mist droplets can be accomplished with combinations of coarse wet and fine dry fiber beds. Fibers such as Dynel are commercially obtainable in diameters down to 10 microns and may be substituted for glass to give results comparable to those cited.

For tests with fluoride fume, crystals of NH_4FHF were evaporated on a hot-plate and the vapor condensed rapidly in the main air stream of the collector. The resulting fume had a median size by weight of 0.54 microns, a geometric standard deviation of 2.08 and it is very hygroscopic. In spite of its hygroscopic character, retention time in the scrubber is too brief to permit maximum growth of particles by adsorption of moisture. Consequently, fine diameter fibers are required for high efficiency collection. How much of an efficiency increase (when operating wet) can be attributed to growth of the nygroscopic fume particles and how much to moistening of the final dry pad by droplet carry-over was not determined, but wet operation appears to be of value in the treatment of hygroscopic fumes.

The most significant gains in efficiency are achieved by reducing the

size of the fibers in the final dry pad. As in the tests with fluoride mist virtually complete removal of the fume was obtained by the use of 1 to 3 micron glass fibers in the final dry pad. Using only HF resistant materials, >98% efficiency was obtained with 15 micron Dynel fibers in the final dry pad (Test C, Table I). When HF-resistant fibers such as Dynel, Saran, polyethylene, etc. are available in sizes below 5 microns they can be expected to produce results comparable to those obtained with the glass fibers. Efficiency of the wetted Neva-Clog screen was >80% for the fluoride fume indicating that it can be used effectively as a primary treatment stage when scrubbing gases containing large quantities of inert dusts.

An $AlCl_3$ fume, generated by heating crystals on a hot plate in the same manner as described above for fluorides and with particle size approximately the same, was removed at an efficiency of 67.2% for the wet stages and an over-all efficiency of 90.5% (Test E, Table I). Considerable improvement in over-all efficiency may be obtained by substituting all 3 micron glass fibers for the 29 micron Saran fibers in the final dry pad. However, for atmospheric pollution control an effluent concentration of <40 mg./m^3 should be satisfactory.

H_2SO_4 mist was generated by evaporating acid on a hot plate and causing it to recondense in the main air stream of the collector. This gave a median size by weight of 0.6 to 0.7 microns. In addition, some tests were conducted using a dilute mist generated by atomizing a 10% aqueous solution of H_2SO_4. This latter method produced a coarse mist having a median drop size by weight of 4.5 microns which is collected at greater than 98% efficiency with two 78 micron diameter Saran wet cells and a 3 micron glass fiber dry cell in series. This same arrangement of scrubbing stages gives 81.4% efficiency for H_2SO_4 generated by dropping and evaporating 10% sulfuric acid on the hot-plate (median size 0.7 micron) and 83.7% for mist generated from 96% acid

(median size 0.6 micron). The reason for the somewhat greater efficiency with the smaller size mist may be attributed to the greater rate of growth of the concentrated H_2SO_4 mist droplets while passing through the wet stages (the two wet stages together are less than 30% efficient in both cases). The dilute acid in contact with the evaporating water is presumed to be of greater initial size. Increasing the quantity of 3 micron glass fibers four-fold in the final dry pad increased over-all efficiency to 94.2%; while adding a 1/2 inch layer of $<$ 1 micron glass fibers to the final Saran fiber dry pad increased efficiency from 83.7 to 96.4% (Test D, Table I). However, the fine fibers had poor fluffing and packing characteristics and resistance rose from 4.5 to 8.5 inches of water gage in about 1 hour.

When efficiencies approaching 100% are required for the treatment of very fine fumes or mists, the fine fibers may be dispersed with sufficient coarse fibers to form a high efficiency bed (small diameter fibers) which will have excellent dimensional stability to resist matting and plugging (large diameter fibers). Such filters can be constructed by (1) carding large and small diameter fibers together to form a homogeneous batt or (2) flocking a preformed large diameter fiber bed with the finer fibers.

5. Absorption Efficiency of Packings

When (as in Table III) the heights of a transfer unit for various sizes of Raschig rings and Berl Saddles are compared with the HTU of a 4 inch deep bed of 78 micron diameter curled Saran fibers packed to a density of 3.6 pounds per cubic foot, it can be noted that 78 micron curled fibers are 5 to 10 times more effective than the Berl Saddles or Raschig rings for absorption. The explanation for the good results obtained with wetted fibers is the very large wetted surface available for absorption. Further, not only is a given height of fibers 5 to 10 times more effective for absorption, but the total weight of the packing, transfer unit for transfer unit, is 75 to 150 times as great for the saddles, (thereby requiring larger, stronger and

more expensive housing for the saddles). This is shown in Table IV.

The design of a scrubber for the concentration and recovery of high concentrations of HF should be based on a stage countercurrent system with concurrent wetting of the packing in each stage. The HF laden air or gas would enter the first stage and be scrubbed concurrently by a relatively concentrated solution of HF. It would then pass through successive stages to be scrubbed by successively weaker HF solutions. Clean water would be introduced at the final scrubbing stage and be pumped forward, stagewise, toward the initial scrubber. In this design concurrent scrubbing is used in combination with countercurrent flow through the apparatus to concentrate HF and strip the air or gas stream.

Design of equipment for the elimination of low concentrations of HF prior to discharge (as a means of preventing atmospheric pollution) can proceed along much simpler lines using the data accumulated in this study. Since only one or two stages would be required for scrubbing stack gases, this method of gas absorption is of general utility for the absorption of other gases as well as HF.

REFERENCES

(1) First, M. W., et al, "U.S.A.E.C. Report No. NYO-1581, Waste Disposal," Boston, Harvard School of Public Health, (1952).

TABLE I

Some Typical Efficiency Results*

Description of Scrubber	Aerosol	Inlet Loading mg/cu.m.	Overall Efficiency % by weight	Overall Resistance in. w.g.
A.				
1) 3" depth 178 μ Saran fibers	HF	231	99.2	1.4
2) 4" depth 78 μ Saran fibers each cell wetted with 9.6 gpm of H_2O	gas	742	99.8	
B.				
1) 1" depth 78 μ Saran fibers wetted with 9.6 gpm water	10% NH_4FHF mist	925	98.1	2.6
2) 4" depth 78 μ Saran fibers wetted with 9.6 gpm water				
3) 2" depth 29 μ Saran fibers (dry)				
C.				
1) Neva-Clog Screen wetted with 9.6 gpm	NH_4FHF fume	53	98.8	5.4
2) 4" depth of 51 μ Dynel (Dry)				
3) 2" depth of 18 and 14 μ Dynel fibers (Dry)				
D.				
Same as B above with addition of 1/2" layer of 1 - 3 μ glass fibers to final dry pad	H_2SO_4 mist	231	96.4	5.2
E.				
Same as D above	$AlCl_3$ fume	400	90.5	5.2

* Air velocity = 108 fpm for all results cited.

TABLE II

Efficiency of Neva-Clog Screen for Collection of Inert Mineral Dusts

Aerosol	Inlet loading gms/cu.m	Water rate gpm/sq.ft.	Air rate cfm/sq.ft.	Mean weight Efficiency %
Atmospheric dust (0.5 μ)	.0001 - .001 (est.)	3.5	108	44.0
Silica (4.1 μ)	0.4 - 1.3	3.5	108	83.3
	0.1 - 0.5	3.5	216	87.2
Talc (1.4 μ)	0.2 - 2.0	3.5	108	79.0
	0.3 - 0.7	3.5	216	85.1

TABLE III

Absorption Efficiency of Packing Materials

Packing	Height of a Transfer Unit (HTU) Ft.
78 micron curled Saran fibers packed 6.2 lb./cu.ft.	0.14
Berl Saddles- 1/2 inch	0.8
1 inch	0.9
1 1/2 inch	1.5
Raschig Rings 1 inch	0.9
1 1/2 inch	1.5

TABLE IV

Physical Characteristics of Some Gas Absorption Packings

Packing Material	Weight lb./cu.ft.	Surface area sq.ft./cu.ft.	Porosity Fraction Voids	Approximate Cost $/cu.ft.	$/lb.
1/2" Berl Saddles	45	141	0.68	6.75	0.15
1 " Berl Saddles	42	79	0.69	5.90	0.14
1/2" Raschig Rings	65	114	0.53	10.00	0.15
1 " Raschig Rings	45	58	0.68	6.30	0.14
178 μ Saran Fibers	6.2	278	0.94	6.20	1.00
78 μ Saran Fibers	3.2	470	0.97	3.20	1.00
50 μ Saran Fibers	3.2	736	0.96	3.20	1.00

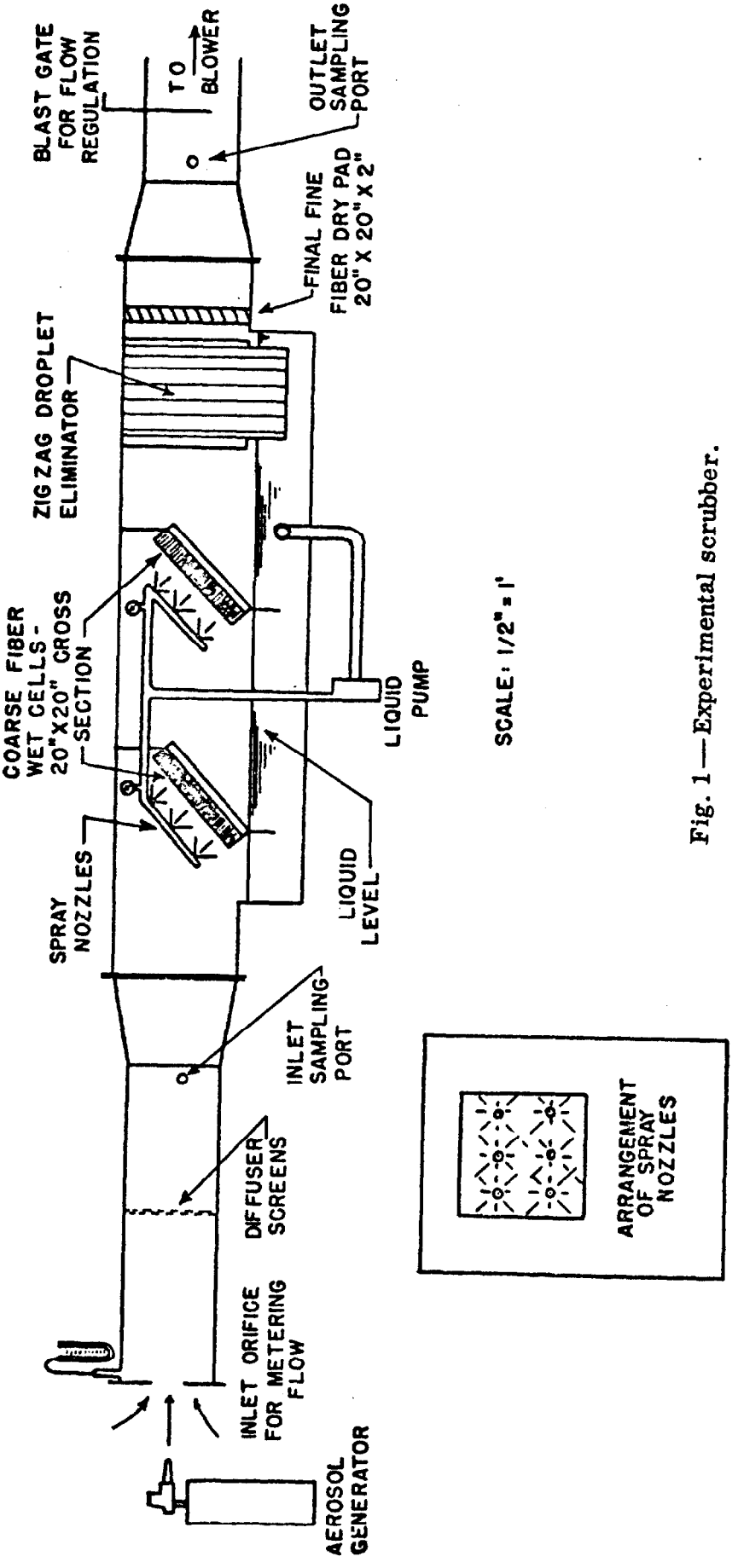

Fig. 1—Experimental scrubber.